ANALYSIS OF UREA FORMALDEHYDE AND UREA-FORMALDEHYDE-ACRYLAMIDE RESINS USING THERMOGRAVIMETRIC METHOD

Zaimatul Aqmar Abdullah[1], Nor Yuziah Mohd Yunus[1*]

[1]Faculty of Applied Science
Universiti Teknologi Mara UiTM Pahang, 26400 Bandar Jengka

[*]Corresponding author: noryuziah@uitm.edu.my

Abstract

Formaldehyde emission reduction in panel products is critical and it can be partially controlled by using resin. As part of the emission reduction exercise, incorporation of acrylamide to urea formaldehyde (UF) was done for UF at molar ratio1.4. The produced UF and UF-acrylamide (UFA) were analyzed using Fourier Transform Infra-red (FTIR) for functional groups identification. Resins were also tested using thermogravimetric analysis (TGA) and the activation energy of both was determined using Kissinger method. The thermal decomposition profile for both samples followed similar trend. Two stages of decompositions were seen, where the first stage decomposed between 100 to 150°C, while the second stage ranges between 200 to 250°C. The low molecular weight material loss and degradation process was well defined. The activation energy was 130-140 kJ/mol for UFA and 150-170 kJ/mol for UF showing the UF resin to be more stable than UFA. Resultant panel product produced using UF and UFA, tested by Desiccator method, gave similar formaldehyde emission.

Keyword: Activation energy-formaldehyde emission-TGA-Urea formaldehyde

Introduction

Urea-formaldehyde (UF) is the most popular resin choice in the aminoplastic and phenoplastic resins category. The UF resin command 80 % share of volume of binders used in the wood composites products. Bonding with UF resins is cheaper compared to phenol formaldehyde resins, and it permits the formation of strong bonds under a wider variety of conditions (Dunky, 1997). UF resin possesses advantages which includes fast and flexible cure, good performance in wood panel, moderate water solubility and colourless glue line.

However drawbacks to the use of UF resin are seen in poorer durability and formaldehyde emission as well as having the lowest moisture resistant among the major wood adhesives (Kim et al., 2006). The reversibility of the amino-methylene linkages and its susceptibility to hydrolysis explains formaldehyde emission.

The durability and stability of UF-bonded wood products could be enhanced by incorporation of flexible co-monomers into the polymers chains. In effort to reduce formaldehyde emission, lower mole ratio UF has been produced which decreased methylol content and increase branching. The resultant resin has lower water sorption, greater inter-chain bonding and decreased flexibility. A variety of modifiers like melamine, furfural alcohol and certain fillers have been examined and some have been found to be beneficial for durability and is currently used in commercial applications. The mechanisms by which these materials act are still being debated. Ebewele et al., (1991) postulated that there is an increase in hydrolytic stability as a result of alteration of polymer network which increased in flexibility. The use of acid based system was also seen to contribute toward lower free formaldehyde in final resin (Edoga, 2006).

In this work, two samples of resins, UF and UF-acrylamide (UFA), were tested using infra-red spectroscopic method and thermal weight loss. Acrylamide choice as modifier stems from presence of amino and amido functions in the monomer which could create crosslinks with methylol-urease during synthesis. It is hoped that acrylamide can be built into the macromolecular network of UF polymer (Duntkiewicz, 1984).

Materials and Methods

Preparation of urea-formaldehyde resins

All UF resins used were prepared in the laboratory, following traditional alkaline-acid, two-step reaction. Formaldehyde (37 wt %) was placed in the reactor and adjusted to pH 7.8 with sodium hydroxide (20 wt %) followed by temperature elevation to 45°C. Subsequently urea was added equally at 1-min intervals, and the mixture was further heated to 90°C and held for 60 min. UF resin with and without acrylamide (3%) were prepared. For formulation with acrylamide, the monomer was added during the first stage just after first urea addition. The second stage of UF resin synthesis involved condensation of the methylolureas. The UF resin was then cooled to room temperature and a second urea charge were added to obtain F/U molar ratio of 1.4.

Resin specifications

Non-volatile Solids Content

About 1 g resin was poured into a disposable aluminum dish and dried in a convection oven at 105°C for 3 hours. Non-volatile solids content was determined by measuring the weight of UF resin before and after drying.

Gel time measurement

Reactivity of UF resins synthesized were gauge using gel time measurement at 100°C using a gel time meter. Formulation used was 100 % resin, with 3% ammonium chloride (NH_4Cl wt 20%) as hardener.

Viscosity

The viscosity of UF resin adhesives were measured at 25°C using a cone-plate viscometer (DV-II +, BROOKFIELD) with no. 2 spindle at 60 rpm. All tests were done in triplicate.

FTIR Spectroscopy Analysis

FTIR of UF and UFA was done on ATR-unit (Attenuated Total Reflectance), with measurements of spectra within a frequency range from 4000-450 cm^{-1}. FTIR allows determining the structure of substances by the interpretation of the frequencies of functional groups to detect the chemical modifications of raw material and mixtures.

Thermogravimetric analysis

Thermogravimetric Analysis (TGA) was used to observe the thermal stability and volatile components in inert nitrogen atmosphere. Thermal analysis of 5-10mg samples was carried out with Q50 thermal analyzer in a Platinum vessel. The furnace temperature is controlled in a pre-programmed temperature/time profile. After calibration, samples measurements were performed from room temperature till up to 500°C at different heating rate (5, 10, 15 and 20°C/min). It should be noted that the kinetic data obtained by TGA are reliable only for irreversible processes, whereas reversible ones are grossly affected by diffusion, and only special procedures can handle them. The analysis was not taken up to full pyrolysis.

The Kissinger method

The TGA data were then analyzed using Kissinger method. The Kissinger method determines kinetic parameters of small milligram quantities of the reacting material by

thermal analysis. A series of heating rates (β) were done to record exothermic peak. The exothermic peak temperature (Tm), assumed as point of constant conversion, is measured at each heating rate. The slope of the line equals −E/R whereas the intercept yields ln[ZR/E] where E is the activation energy, Z is the Arrhenius pre-exponential factor and R is the gas constant (=8.314 J/mol K). A first order reaction (n = 1) reaction order is usually assumed.

Plywood formaldehyde emission

Standard three ply plywood was produced using the UF and UFA resins. After 72 hours conditioning the plywood was cut to 50 x 150 mm samples. The samples were then tested for formaldehyde emission using the Desiccator method for sample collection. Collected emission samples were then analyzed using UV-spectroscopic method based on a yellow complex formed through reaction of formaldehyde with acetyl acetone. Formaldehyde level is obtained by measuring the colour intensity compared to a standard curve.

Result and Discussion

Resin Specifications

Resin specification can be seen in **Table 1**. At end of process both resins were adjusted to pH 8.00. Under similar reaction environment, the UF control showed final viscosity of 637 mPa.s. This indicates higher advancement of pure UF compared to UFA. The UFA also registered a slightly lower resin content which might contribute to the lower viscosity as more solvent is present in the resin. The presence of acrylamide increased the gelation time by 68%, an indication that the acrylamide amine (–NH) functionality gave rise to different reaction mechanism. The crosslinking which occurs during cure of the resin is lowered. It is possible that the –NH functionality has reacted with more free formaldehyde thus lowering the cross linker amount normally present in pure UF. The acrylamide addition is akin to more urea added thus lowering the UFA molar ratio.

Table 1 Specification of UF and UFA

Properties of resin	Unit	UF (control)	UF-A
pH at 25°C		8.0	8.0
Viscosity at 25°C	mPa.s	637	460
Non-volatile Solid content	wt/wt (%)	54.5	52.7
Gel time	s	128	214

FTIR Spectroscopy Analysis

FTIR in values in **Table 2** shows peaks in regions that could identify potential reaction in between acrylamide and UF to produce UFA. The backbone of UF and UFA is the –NH stretching of secondary amide (1), -C=O stretch mode (4) and –CH symmetric stretching mode (2). The –OH groups available in the UF and UFA is also seen in the region of 3329 cm^{-1} (1), sharp and broad.

The acrylamide-NH stretching mode of primary amide differs where it has two medium double peaks at 3335 cm^{-1} and 3172 cm^{-1} (2) which completely disappeared once added to the UFA production. Peaks at 2812 cm^{-1}, 1607 cm^{-1} and 1050 cm^{-1} also could not be found in UFA spectrum. This suggests a reaction had occurred and the acrylamide monomer had become incorporated into UFA.

Peaks cluster from1310 cm^{-1} to 1444 cm^{-1} (6) could be assigned to -CH bending mode in -CH_2, -CH_2OH, and N-CH_2-N. Comparison of UF and UFA revealed the absence of peaks 1444 cm^{-1} and 1310 cm^{-1}. These peaks removal could be due to the reaction of acrylamide

with –NH functions thus removing primary amine structure from control UF. Another missing peak was at 1093 cm^{-1} (8) which originated from combined methylol C-O stretch and amide C-N stretch mode. This disappearance could be due to UFA not experiencing the –OH deformation in $–CH_2OH$. Acrylamide functionality –NH cause bigger hindrance to the UFA chain and create a more rigid structure. In term of molecular structure acrylamide (C_3H_5NO) is bigger than formaldehyde (CH_2O).

Table 2 Summary of the absorption wavenumber for acrylamide, UF and UFA

Functional Group* **w-weak, m-medium, s-strong, b-broad**	**Peak Value (cm^{-1})** **Acrylamide**	**Peak Value (cm^{-1})** **UF**	**Peak Value (cm^{-1})** **UFA**	**No**
NH stretching mode of secondary amide OH stretching mode		3329s,b	3329s,b	1
NH stretching mode of primary amide	3335m, 3172m			2
C-H symmetric stretching mode of CH_2	2812w	2958w	2958w	3
C=O stretching mode	1659s	1633m	1626m	4
N-H bending mode of aliphatic secondary amide	1607s	1541s	1537s	5
C-H bending mode in CH_2 , CH_2OH, N-CH_2-N	1350-1424m	1310-1444m	1358-1380m	6
N-CH_2-N asymmetric stretching mode	1135w	1133w	1127w	7
C-O stretching and C-N amide stretching mode	1050w	1093w		8
NH stretching mode of primary amide	959mb, 985mb	999sb	1011sb	9
NH stretching mode of secondary amide	839mw	882mw	773mw	10

*Source: (Silverstein, 2005)

Thermogravimetric Analysis

In both **Figure 1** and **Figure 2** the small peak that appeared for all sample is typical for methanol evaporation temperature range as the formaldehyde used have some residual methanol due to incomplete conversion of methanol to formaldehyde. Addition of methanol to formalin for stabilization and improved storage is common in order to reduce settlement of paraformaldehyde.

Two major degradation stages were seen for all samples. The stage of degradation (Stage I) between 100 to 150°C is mainly attributed to the removal of entrapped residual water (Poljansek, 2006) and the elimination of free formaldehyde monomer. Both material evaporates in the range of 99-102ºC and could not be fully distinguished. At this stage the presence of heat will also encourage water loss due to curing or polymerization of UF and UFA (Li et al., 2014). The second stage of degradation stage (Stage II) between 200 to 250°C is the decomposition of UF and UF-acrylamide cross-linked polymer formed by the urea, formalin and acrylamide polymerization (Burrows, 1981). According to Li et al., (2014), further weight reduction occurs via formaldehyde emission which resulted from crosslinking reaction and degradation of hydroxyl-methyl and methylene group.

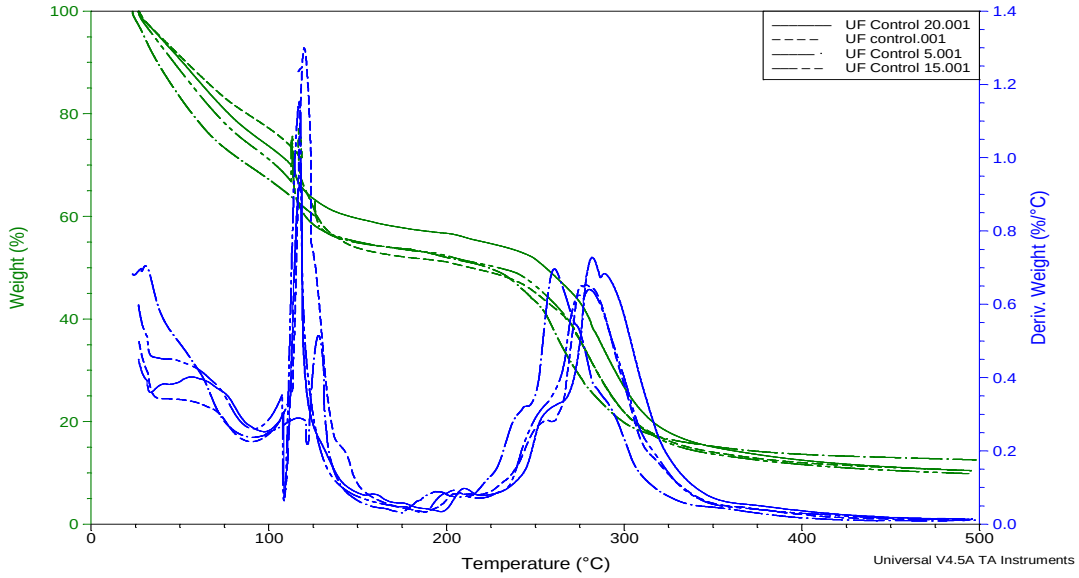

Figure 1 Decomposition process of Control UF resins at a heating rate (5, 10, 15 and 20°C)

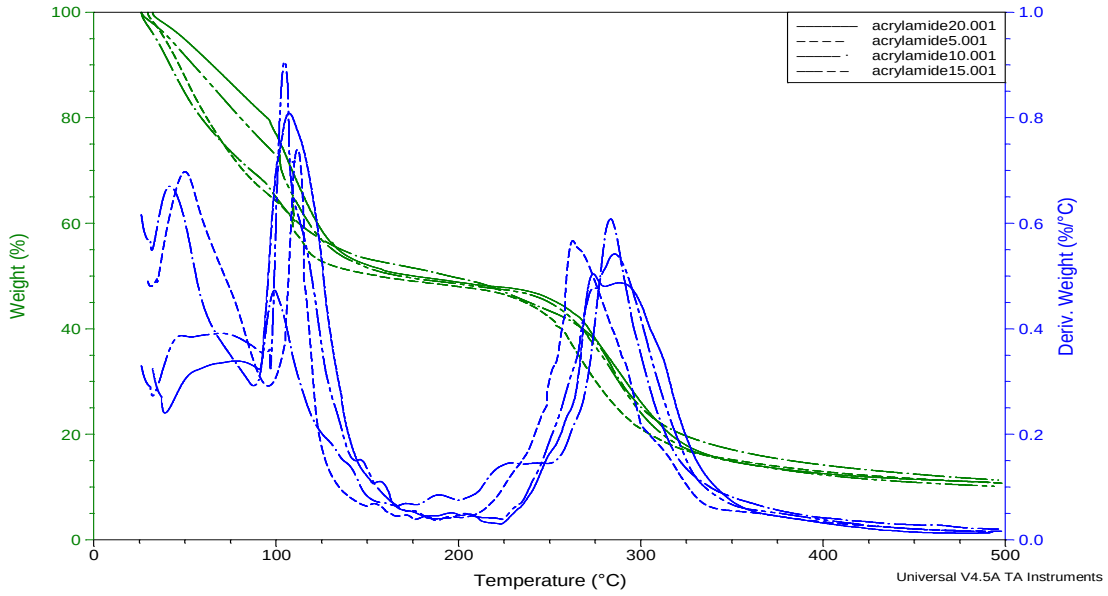

Figure 2 Decomposition process of UFA resins at a heating rate (5, 10, 15 and 20°C)

The peak temperatures of each stage are summarized in **Table 3**. The first (1st) peak temperature on average is higher for UF by 10 to15% at all rates except for 10ºC/min. The initial decomposition temperature decreases as heating rate increased (Lee et al., 2003). The removal of entrapped residual water and elimination of free monomer seems easier in UFA, an indication of lower polarity of UFA. The second peak showed the UFA having higher peak by 1-2 %. For the same area at heating rate of 20ºC/min, two peaks appeared but it still

follows the same quantum trend. Interestingly, at decomposition stage of crosslinked matter (2^{nd} peak) the temperature of degradation occurs at similar value. The behavior of the curve is also related to the single step process of resin making where less branching will be seen in the resin (Janović et al., 2011).

Table 3 Decomposition characteristics of the UF resin: peak temperatures, weight loss and residue percentages obtained from different heating rate

Resin	Heating rate (°/min)	T_p 1st peak (°C)	T_p 2nd peak (°C)	TWL (%)	Weight Residue (%)
UF	5°C	128.42	260.92	43.71	56.29
	10°C	120.14	278.98	64.07	35.93
	15°C	117.13	281.60	52.88	47.12
	20°C	117.13	281.99	52.94	47.06
			(~290)		
UFA	5°C	111.86	262.42	46.86	53.14
	10°C	99.48	283.87	45.58	54.42
	15°C	104.33	286.97	54.08	45.92
	20°C	107.34	272.96	63.17	36.83
			(~290)		

T_p = peak temperature, TWL = total weight loss (degradation of stage 1 & 2)

Table 4 shows the apparent activation energy values calculated for both resins with data obtained via Kissinger Method plot as seen in **Figure 3**. Activation energy represents the height of the potential or energy barrier separation that needs to be overcame moving from reactants to products in a reaction. The value observed as E_a for control UF resin was in range of 150-170 kJ/mol as opposed to E_a of UFA resin at 130-140 kJ/mol. UF resin higher activation energy implicates the stability of the bonding of the UF resin, which confirms the degradation pattern shown earlier especially the first peak, which is 10 to 15% higher than UFA.

Comparison of the TGA decomposition data of UF acryl amide and UF control shows that UFA is less stable (10, 15 and 20°C) compared to the UF control. However it is a very small scale and it shows that UF control itself is already stable. This was indicated by the lower peak degradation temperature (Janović et al., 2011). The easier degradation of UFA coupled with slower crosslinking makes the UFA less attractive compared to standard UF.

Table 4 Apparent activation energy of control UF resin and UFA resin

Type of resin	T_1P E_a (kJ/mol)	T_2P E_a (kJ/mol)
UF	166.67	153.27
UFA	134.73	136.60

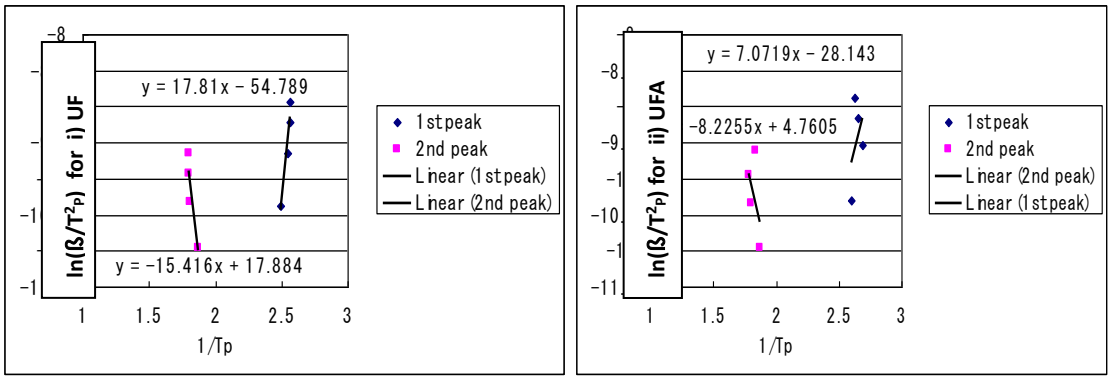

Figure 3 Activation Energy of i) Control UF and ii) UFA (Kissinger Method)

Formaldehyde emission from plywood

The formaldehyde emission for plywood made using UF and UFA was 0.28 and 0.25 mg/L respectively. Even though the reading of UFA is 10% lower than UF, it was not a substantial lowering in emission after incorporation of acrylamide for the resin produced. The presence of acrylamide in resin effected the gelation time severely (68 %) but does not contribute to the lowering of emission. The reduction in reactivity may have contributed to improper glue curing during plywood making. More tests should be made using different press time comparing the UF and UFA before conclusion on whether the acrylamide incorporation has an impact on the formaldehyde emission reduction in plywood.

Conclusion

FTIR analysis was able to detect incorporation of acrylamide to UF. TGA thermal decomposition profile of UF and UFA shows similar trends as a single charge process backbone was used in each reaction. The second stage decomposition of UF and UFA resin in range 200 to 250°C was used to calculate the activation energy for both samples. The Kissinger Method calculation showed activation energy in the range of 130-140 kJ/mol for UFA and 150-170 kJ/mol for UF control. It was obvious that between these 2 samples, the control UF resin is more stable compared to the acrylamide modified UF.

Acknowledgement

-

Conflict of interests

-

References

Burrows, H. D., Ellis H. A. & Utah S. I. (1981). Adsorbed metal ions as stabilizers for the the rmal degradation of polyacrylamide. *Polymer,* 22(12), 1740-1744.

Dunky, M. (1997). Urea-formaldehyde (UF) adhesive resins for wood. *International Journal of Adhesion and Adhesives*, 18, 95-107.

Duntkiewicz, J. (1984). Preparation of cured urea-formaldehyde resins of low formaldehyde e mission. *Journal of Applied Polymer Science,* 29, 45-55.

Ebewelle, R. O., Myers, G. E., River B. H. & Koutsky J. A. (1991). Polyamine modified urea -formaldehyde resins. 1. Synthesis, Structure and Properties. *Journal of Applied Polymer Scie*

nce, 42, 2997-3012.

Edoga, M. O. (2006). Comparative Study of Synthesis Procedures for Urea - Formaldehyde Resins (Part I. *Leonardo Electronic Journal of Practices and Technologies,* (9), 63-80.

Janović, S. S., Janović, V., Konstantinović, S, Marković, G. & Concović, M-M. (2011). Ther mal behavior of modified urea formaldehyde resins. *Journal of Thermal Analysis and Calori metry,* 104(3), 1159-1166.

Kim, J, Carlborn, K., Matuana, L. M. & Heiden, P. A. (2006). Thermoplastic modification of urea-formaldehyde wood adhesives to improve moisture resistance. *Journal of Applied Polym er Science,* 101, 4222-4229.

Lee K-y., Kim, D-j., Kim, H-j., Hwang, T-s., Rafailovich, M. & Sokolov, J. (2003). Activatio n energy and curing behaviour of resole- and novolac-type of phenolic resins by differential s canning calorimetry and thermogravimetric analysis. *Journal of Applied Polymer Science,* 89 , 2589-2596.

Li, B., Zhang, J.-z., Ren, X.-y., Chang, J.-m., & Gou, J.-s. (2014). Preparation and characteriz ation of bio-oil modified urea-formaldehyde wood adhesives. *BioResources,* 9(3), 5125-5133

Poljansek, I., Sebenik, U. & Krajnc, M. (2006). Characterization of phenol–urea–formaldehy de resin by inline FTIR spectroscopy. *Journal of Applied Polymer Science,* 99, 2016-2028

Silverstein, R. M., Webster, F. X., & Kiemle, D. J. (2005). Spectrometric Identification of Org anic Compounds. 7th Edition. Wiley and Sons. Canada. Pp. 72-126